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IMPROVED GLASS COMPOSITIONS FOR IMMOBILIZATION OF SRP WASTE

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INTRODUCTION

Radioactive waste produced from reprocessing nuclear materials for defense programs at Savannah River Plant (SRP) is stored in large underground tanks on the plant site. This alkaline waste is made up of water soluble salts and insoluble "sludges." Most of the waste actinides and fission products are contained in the insoluble sludge, consisting mainly of hydroxides and hydrous oxides of iron, aluminum, and manganese. The rest of the waste is either in the form of a soluble crystalline salt cake or a nearly-saturated supernatant salt solution. This fraction contains about 95% of the fission product cesium and traces of other radionuclides.

Methods to immobilize SRP waste for long-term storage are being developed at Savannah River Laboratory (SRL). In the current reference process (Figure 1), the supernatant liquid is pumped from the tanks and decontaminated by ion exchange. The sludge is slurried with water, removed from the tank, and washed with hot caustic to remove about 75 wt % of the aluminum. The sludge is then water-washed to remove soluble salts. The cesium-loaded zeolite from ion exchange are then mixed with the sludge.

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The radioactive sludge, cesium-loaded zeolites, and residual radionuclides from ion exchange are dried by spray calcination, mixed with pre-melted glass frit, and melted to form a borosilicate glass in a joule-heated melter. The molten glass is poured into a steel canister and allowed to cool. Table 1 shows the composition of the average calcine and extreme compositions expected.

Initial glass composition development was directed toward demonstrating the feasibility of immobilizing SRP waste in glass. A large amount of experimental data was obtained on the properties of simulated and actual waste immobilized in glass made from Frit 21 (Table 2). In laboratory tests, this frit formed durable glasses containing 35 wt % sludge which spanned the range of compositions found in SRP wastes. Therefore, Frit 21 was chosen for large-scale testing.

However, results with large-scale tests with simulated SRP waste indicated several problems:

- Melting rates were low.
- A persistent foam formed during melting, which slowed melting.
- A ferrite-spinel slag formed at the bottom of the melter.
- A stable foam was generated when a cooled melt was reheated (reboil).

Experiments at SRL have indicated that these results can be alleviated by the following methods.

1. Increasing melt temperature.
2. Reducing sludge loading.
3. Adequate mixing of frit and waste.
4. Improving glass compositions.

The first three methods are costly and might cause other processing problems. Higher melt temperatures would increase the volumes of off-gas. Reduced loading would increase glass production. Longer mixing would cause excessive dusting. Therefore, the effects of frit composition on both process and product quality were studied in detail.

Discussion

The processing variables studied were viscosity and waste solubility (primarily ferrite solubility); the product quality variables studied were leachability, and devitrification during cooling.

Viscosity

As reported previously,[1,2] the viscosity is mainly controlled by the ratio of the moles of alkali oxide to moles of silica in the frit, and by the mole fraction of Li_2O in the alkali oxide. However, increasing the B_2O_3, alkaline earth, or TiO_2 content of the frit also reduced viscosity slightly.

Waste Solubility

Ferrite solubility is affected most by the B_2O_3 and the TiO_2 content of the frit. As Figures 2 and 3 show, B_2O_3 increases, and TiO_2 decreases ferrite solubility. However, small additions of TiO_2 do increase actinide solubility. Also, the effect of B_2O_3 was not as great on high-alkali frits as on lower alkali frits. Additives to improve leachability, such as ZrO_2 or La_2O_3, also greatly reduced ferrite solubility; 1 wt % of either in the frit increased the temperature at which the average sludge composition was soluble (liquidus temperature) by about 50°C.

Leachability

Leachability is sensitive to frit composition. Variations in all components can have large effects. Substitution of Li_2O for Na_2O on a molar basis dramatically reduces the leach rate of the glass in a variety of media. Increasing the B_2O_3 content of the frit increases the leach rate in acid, but decreases the leach rate in alkali. Substitution of MgO for CaO also reduces the leach rate, especially in acid. Small additons of ZrO_2, TiO_2, or especially La_2O_3 reduce leach rate.

Devitrification During Cooling

Li_2O or TiO_2 in the frit promotes devitrification; B_2O_3 inhibits it. Table 3 shows an almost linear correspondence between the extent of devitrification and the TiO_2 content of the frit. The effect of Li_2O is probably kinetic because the viscosity of the glass between 600 and 900°C is very low.

Improved Frits

Based on these tests, two improved frits were designed, Frits 211 and 131 (Table 2). Frit 211 was derived from Frit 21 simply by eliminating TiO_2. Table 4 summarizes preliminary tests of the simulated waste glasses. The leach rates of glass from Frit 211 are comparable to glass from Frit 21, but the waste solubility, tendency to devitrify, and viscosity of Frit 211 glasses are better. In tests in a small-scale continuous joule-heated melter, Frit 211 dissolved simulated waste twice as fast as Frit 21. Frit 211 is now being used in large-scale tests using simulated waste, and small-scale tests using actual waste.

Frit 131 contains more B_2O_3 and less TiO_2 to increase waste solubility. A small amount of TiO_2 has been retained to increase actinide solubility and to reduce leachability. The molar ratio of Li_2O to total alkali has been increased to further improve leachability. MgO has been substituted for CaO to improve leachability and waste solubility in the glass. ZrO_2 and La_2O_3 increase leach resistance.

REFERENCES

1. M. J. Plodinec, "Development of Glass Compositions for Immobilization of SRP Waste," USDOE Report DP-1517 (1979).
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Table 1. Major Components of SRP Waste Calcines, wt % (after 75 wt % Al removal)

	High Aluminum	High Iron	Average
Fe_2O_3	14.80	55.90	47.16
Al_2O_3	50.77	1.29	9.24
MnO_2	12.16	3.74	12.98
U_3O_8	3.57	12.98	4.25
CaO	0.97	3.80	3.51
NiO	2.17	9.54	5.84
SiO_2	1.57	--	1.12
Na_2O	5.41	4.75	6.63
Na_2SO_4	--	1.21	--
Zeolite	8.58	8.00	8.05

Table 2. Frit Compositions, wt %

	Frit 21	Frit 211	Frit 131
SiO_2	52.5	58.3	57.9
B_2O_3	10.0	11.1	14.7
Na_2O	18.5	20.6	17.7
Li_2O	4.0	4.4	5.7
CaO	5.0	5.6	--
MgO	--	--	2.0
TiO_2	10.0	--	1.0
ZrO_2	--	--	0.5
La_2O_3	--	--	0.5

Table 3. Effect of TiO_2 On Devitrification During Cooling

TiO_2 Content of Frit, wt %	0	5	10
Temperature to get to 5% Crystals, °C	930	1000	1030
Devitrification After Cooling, vol %	10	50	90

Table 4. Frit 211 Compared to Frit 21

Property	Frit 21	Frit 211
Leach Rate at pH 4.4, wt %	0.31	0.23
Leach Rate at pH 11.5, wt %	0.23	0.46
Tendency to Devitrify	High	Moderate
Viscosity, poises	22	13
Waste Solubility at 1150°C, Max. Loading - Calcine	25	30
Melting Rate, g/min	4.1	9.8

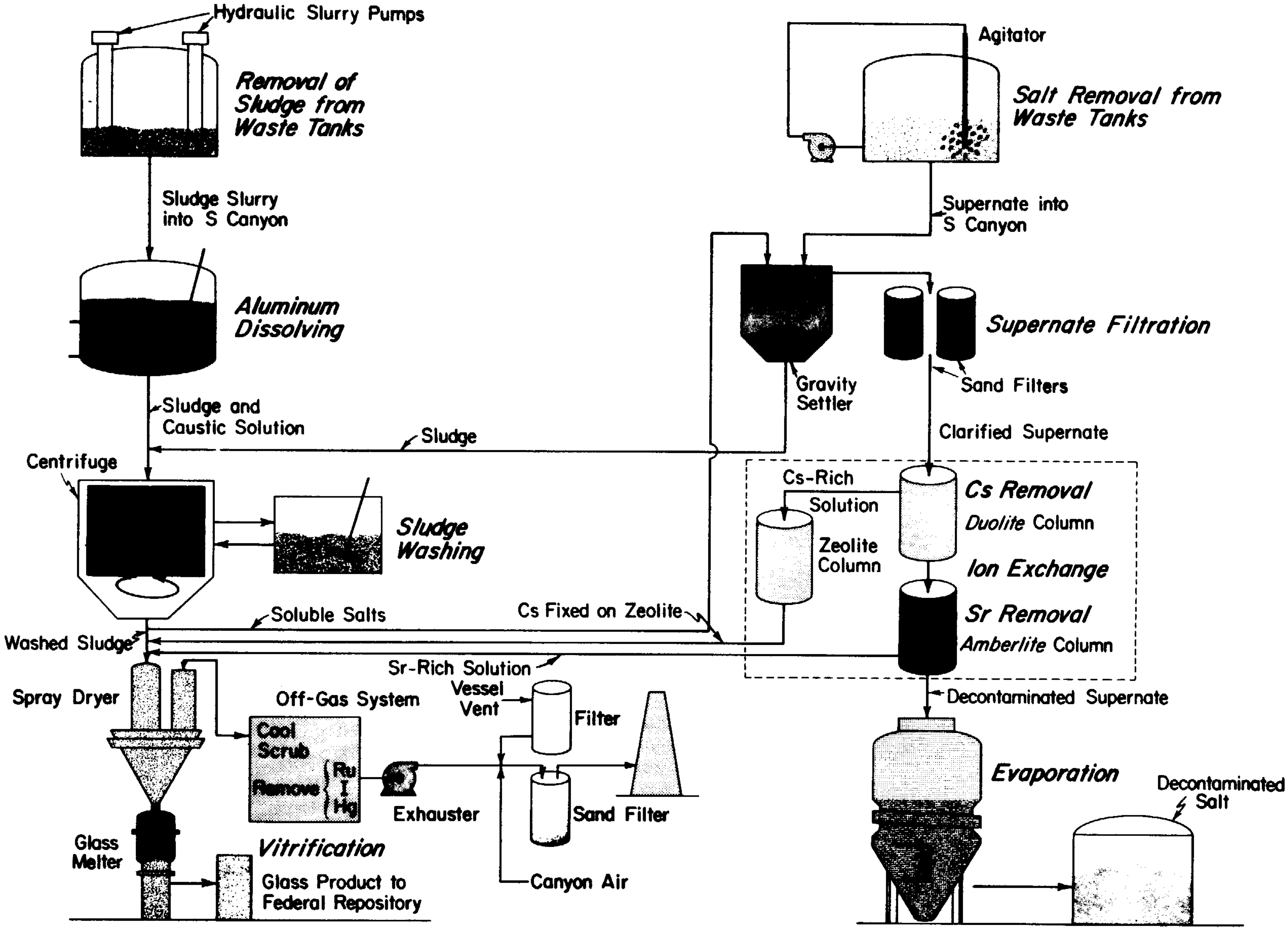

FIGURE 1. Reference Process for Immobilization of SRP Waste

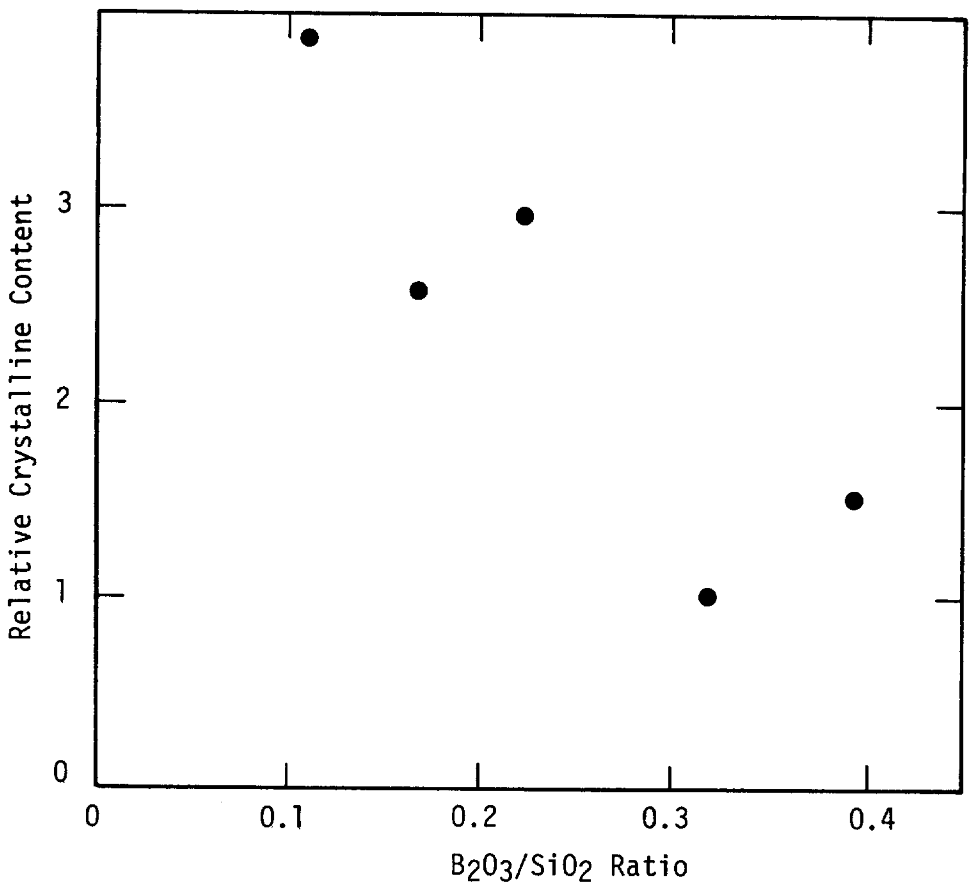

FIGURE 2. Effect of B_2O_3 on the Crystalline Content at 1000°C

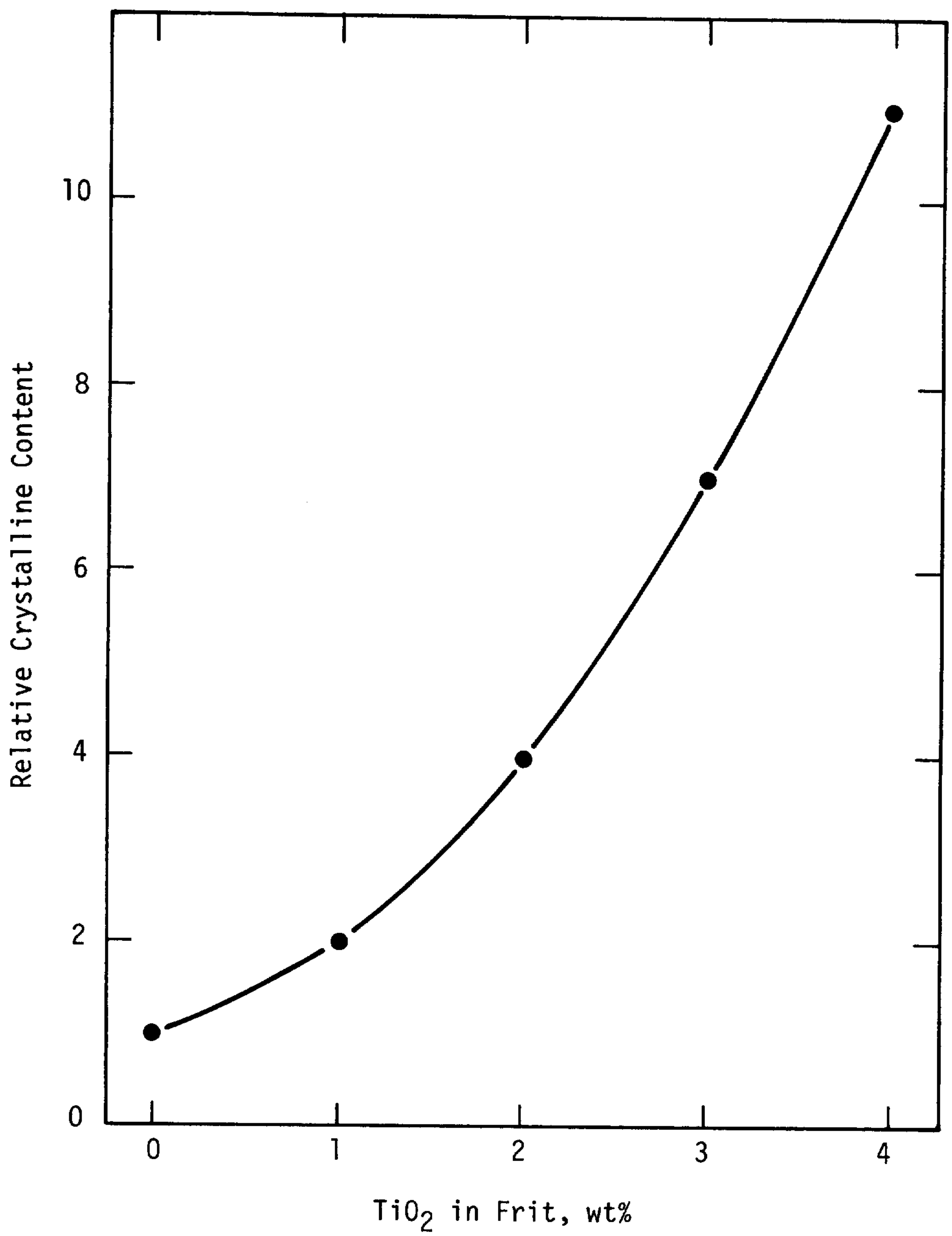

FIGURE 3. Effect of TiO_2 on the Crystalline Content at 1000°C